THERMAL CONDUCTIVITY OF GASES UNDER HIGH PRESSURE

BY

MARVIN FREEMAN NATHAN

B.S., The Pennsylvania State College, 1943

M.S., University of Illinois, 1945

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING IN THE GRADUATE COLLEGE OF THE UNIVERSITY OF ILLINOIS,

1948

URBANA, ILLINOIS

1948

THERMAL CONDUCTIVITY OF GASES UNDER HIGH PRESSURE

BY

MARVIN FREEMAN NATHAN

B.S., The Pennsylvania State College, 1943

M.S., University of Illinois, 1945

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMICAL ENGINEERING IN THE GRADUATE COLLEGE OF THE UNIVERSITY OF ILLINOIS,

1948

URBANA, ILLINOIS

1948

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Professor E. W. Comings for his many suggestions and encouragement during the course of this investigation, to the Pan American Refining Corporation for providing a fellowship under which the last year's work was completed, and to Mr. E. H. Vause for his valuable assistance during the experimental work.

THERMAL CONDUCTIVITY OF GASES UNDER HIGH PRESSURE

INTRODUCTION

The increasing use of high pressure gas-phase processes has made necessary a knowledge of the effect of pressure on the physical properties of gases. Many pressure-volume-temperature measurements for the common gases, as well as equations of state and compressibility factor correlations for these are available. Bridgman (1) and Comings (4) list and evaluate these data. Within the last few years a considerable amount of high pressure gas-viscosity data have appeared. Comings, Mayland and Egly (5) summarized the viscosity data available and correlated the viscosity ratio as a function of reduced temperature and reduced pressure.

Only a small amount of thermal conductivity data are available because of the difficulties involved in measuring this property. These data indicate (11, 12) that the variation of thermal conductivity with pressure is of the same order of magnitude as the change of viscosity with pressure. A knowledge of the thermal conductivity of gases under high pressure would be useful in the design of heat transfer equipment and in certain other fundamental respects. The Chilton-Colburn (3) analogy relating heat and mass transfer permits the prediction of mass transfer coefficients of gases under high pressure if the thermal conductivity and certain other properties are known.

The purpose of this work was to obtain a correlation showing the effect of pressure on the thermal conductivity of gases and to obtain experimental data to compare with the predicted values.

CORRELATION OF THERMAL CONDUCTIVITY RATIO

Enskog's (2, 7) theoretical equations have been used to prepare a correlation of the thermal conductivity ratio. The thermal conductivity ratio is defined as the ratio of the ther-

mal conductivity at a temperature, t, and pressure, p, to the thermal conductivity at the same temperature, t, and at atmospheric pressure. It was shown by Comings, Mayland and Egly (5) that the thermal conductivity ratio is a function of reduced pressure and reduced temperature and the correlation is made on this basis. The literature on the determination of the thermal conductivity of gases under high pressure has been reviewed. Only the data of Vargaftik (12) seem valid. Vargaftik's data on nitrogen up to 90 atmospheres at 40 and 60°C. agrees within 1 per cent with the correlation.

STEADY STATE METHOD

A. Apparatus

The steady state apparatus was based upon the principle of heat transfer which requires the transfer of the same amount of heat through two layers of different materials in series with each other. These layers were annuli, ½ inch wide and 18 inches long, formed by three concentric steel tubes. Gas was trapped in the pores of a solid insulating material (U. S. Flotofoam (8)) to avoid convection.

Water at 37.2°C. was pumped at a high velocity through the inner steel tube and the whole unit was placed in a constant temperature bath maintained at 52.5°C. These temperatures were controlled to ±0.015°C. The test gas filled the colder layer and air was trapper in the warmer. A calibration curve was obtained with the following gases in the inner annulus at atmospheric pressure: carbon dioxide (99.5% pure), ethylene (99.5% pure), helium (98% pure), hyrdogen (99.7% pure), methane (99% pure), and nitrogen (99.8% pure), by measuring the ratio of the temperature drop over each layer. These calibration curves take into account the constants of the apparatus, the mechanism of heat transfer and radiant heat transfer. High pressure runs up to 119 atmospheres were made at 42.4°C. on nitrogen.

The equation for heat losses to the ends of the bomb was derived and this indicated the necessity for adding heat elec-

trically to each end of the bomb to maintain the sensitivity of the apparatus. Temperatures were measured to ±0.01°C. by means of iron-constantan thermocouples of 28 gauge wire and a Type KII Leeds and Northrup potentiometer.

The test gas was compressed in a nitrogen-mercury pump and compressor, which consisted of two steel cylinders partially filled with mercury and connected at the bottom by high pressure tubing. Compressed nitrogen was admitted to the pump cylinder, forcing the mercury to flow into the compressor cylinder and compressing the sample. The nitrogen was compressed by a three-stage mechanical compressor. The pressure in the bomb was read by two twelve-inch Bourdon gauges, one of which covered the range 0 to 1200 lbs. per sq. in., the other from 1200 to 3000 lbs. per sq. in. These gauges were checked at frequent intervals by means of a dead weight gauge.

B. Results and Discussion

The calibration curves determined on six gases of known thermal conductivity at atmospheric pressure (carbon dioxide, ethlyene, helium, hydrogen, methane and nitrogen) have a precision of ±1 per cent. These calibration curves indicate that parallel heat transfer through the gas and solid in the mixture is the controlling mechanism and is accompanied by some series heat transfer. The results obtained by this investigation for nitrogen at 42.4° C. at 1 to 119 atmospheres do not agree with the results of Vargaftik at 40°C. nor do they agree with the values from the correlation based on Enskog's equations. The data obtained in this work are from 5 to 40 per cent higher than Vargaftik's data. The percentage error increases as the pressure increases and also increases with time at a given pressure. The discrepancy between this work and Vargaftik's data is attributed to adsorption and absorption of the gas by the solid insulating material.

An improved modification of the steady state apparatus is suggested which eliminates the need for trapping the gas in the pores of an insulating material. This apparatus is

based on Kraussold's (9) work which showed that heat is transferred by conduction only if the product of the Grashof Group and the Prandtl Number does not exceed 600.

THE UNSTEADY STATE METHOD

A. Apparatus

The unsteady state transfer of heat to an infinite cylinder permits the experimental determination of the thermal diffusivity. The cylinder is brought to a uniform temperature and the surface temperature is suddenly changed. By measuring the change of temperature with time at several points within the cylinder, it is possible to obtain the thermal diffusivity. A knowledge of the heat capacity and density then permits the calculation of the thermal conductivity. Two solutions of the differential equation for unsteady state heat transfer were considered: (1) the solution for the case where the boundary condition is an experimentally determined exponential function of time, and (2) Pigford's (10) solution for a composite cylinder of infinite length. The possibility of using the concept of the equivalent thickness was also considered.

The apparatus consisted of a water jacketed heavy-walled cylinder, 40 inches long and 4.5 inches in diameter. To avoid convection, the test gas was trapped in the pores of a solid insulating material (U. S. Flotofoam (8)). The temperatures were measured by four iron-constantan thermocouples of 28 gauge wire placed on isothermal lines at the following points within the cylinder: (1) at the outer wall, (2) at the inner wall, (3) at a distance half-way between the inner wall and the center line, and (4) at the center line. Two constant temperature baths, one at 53°C. and the other at 47°C. were used to supply the water pumped at a high velocity through the water jacket. A system of quick-opening and closing valves, electrically controlled, allowed the temperature of the water in the jacket to be changed rapidly. Three electric timers capable of measuring time to the nearest 0.1 second were connected to

the circuit which controlled the valves. In this way all three timers could be started simultaneously with the change in temperature of the water flowing through the water jacket.

The temperature measuring system, the pressure measuring system, and the auxiliary high pressure apparatus were the same as that described for the steady state apparatus. Data for calibration curves were obtained at atmospheric pressure for the gases described previously.

B. Results and Discussion

It was found experimentally impossible to bring the surface of the cylinder to its final temperature rapidly enough to make use of Pigford's solution for a composite cylinder. However, the surface boundary condition could be written as an exponential function of time and the solution for this case was used.

The high heat capacity of the thermocouple as compared to the heat capacity of the gas it displaced caused a time lag in the thermocouple. A method was developed for correcting this error. This method, however, resulted in large errors in the experimental thermal diffusivity for small experimental errors. There was evidence which seemed to point to adsorption and absorption in the apparatus at atmospheric pressure. The method was abandoned when the apparatus developed a leak at elevated pressures.

SUMMARY

A correlation for the thermal conductivity ratio based on the theoretical equations of Enskog and on the theorem of corresponding states has been made. This correlation may be used to predict the thermal conductivity of pure gases and vapors at high pressures when the thermal conductivity at atmospheric pressure and the critical temperature and pressure are known.

A pressure-thermal conductivity isotherm for nitrogen at 42.4°C. has been determined experimentally for pressures

from 1 to 119 atmospheres. The data is from 5 to 40 per cent higher than that obtained by Vargaftik and also than that predicted by the correlation. This discrepancy is attributed to adsorption and absorption of the gas by the porous plastic material used in the bomb to eliminate convection. Accurate data on the thermal conductivity of gases under high pressures are still needed to substantiate the correlation. Until those data are available, the correlation presents the best means of predicting thermal conductivities of gases under high pressure.

An apparatus and method are described which will avoid the sources of error encountered in this investigation.

BIBLIOGRAPHY

1. Bridgman, P. W., **Rev. Mod. Phys., 18, 1** (1946).
2. Chapman, S. and Cowling, T. G., "Mathematical Theory of Non-Uniform Gases", Chap. 16, MacMillan Company, Cambridge (1939).
3. Chilton, T. H. and Colburn, A. P., **Ind. Eng. Chem., 26,** 1183 (1934).
4. Comings, E. W., **Ind. Eng. Chem., 39,** 948 (1947).
5. Comings, E. W., Mayland, B. J. and Egly, R. S., University of Illinois Eng. Expt. Sta. Bull. 354 (1944).
6. Comings, E. W. and Nathan, M. F., **Ind. Eng. Chem., 39,** 964 (1947).
7. Enskog, D., **Kungl. Svenska Vetenskaps. Akademiens Handl., 63,** No. 4 (1921).
8. "Flotofoam" manufactured by the U. S. Rubber Company and described in a paper presented by Van Buskirk, E. C. and Surland, C. C., at the New Orleans, La., Meeting of the A. I. Ch. E., Feb. 17, 1948.
9. Kraussold, H., **Forsch. Gebiete Ingenieurw., 5B,** 186 (1934).
10. Pigford, R. L., personal communication (1947).
11. Sellschopp, W., **Forsch. Gebiete Ingenieurw., 5B,** 162 (1934).
12. Vargaftik, N., **Teck. Phys. U. S. S. R., 4,** 343 (1937).

VITA

The author was born in New York City on March 13, 1922. He attended the public schools of Allentown, Pennsylvania, and graduated from Allentown High School in 1940. In the fall of 1943, having completed his undergraduate work, he received a Bachelor of Science Degree from The Pennsylvania State College. Immediately thereafter he entered the Graduate School of the University of Illinois where he held appointments as a teaching assistant, N. D. R. C. Special Research Assistant, and Pan-American Refining Corporation Research Fellow. From this University he received a Master of Science Degree in 1945. He is co-author of a paper entitled "Thermal Conductivity of Gases at High Pressures" which was published in "Industrial and Engineering Chemistry," Vol. 39, pp. 964-970, August, 1947.